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Gas-Phase Excited State Dynamics of Bithiophenes

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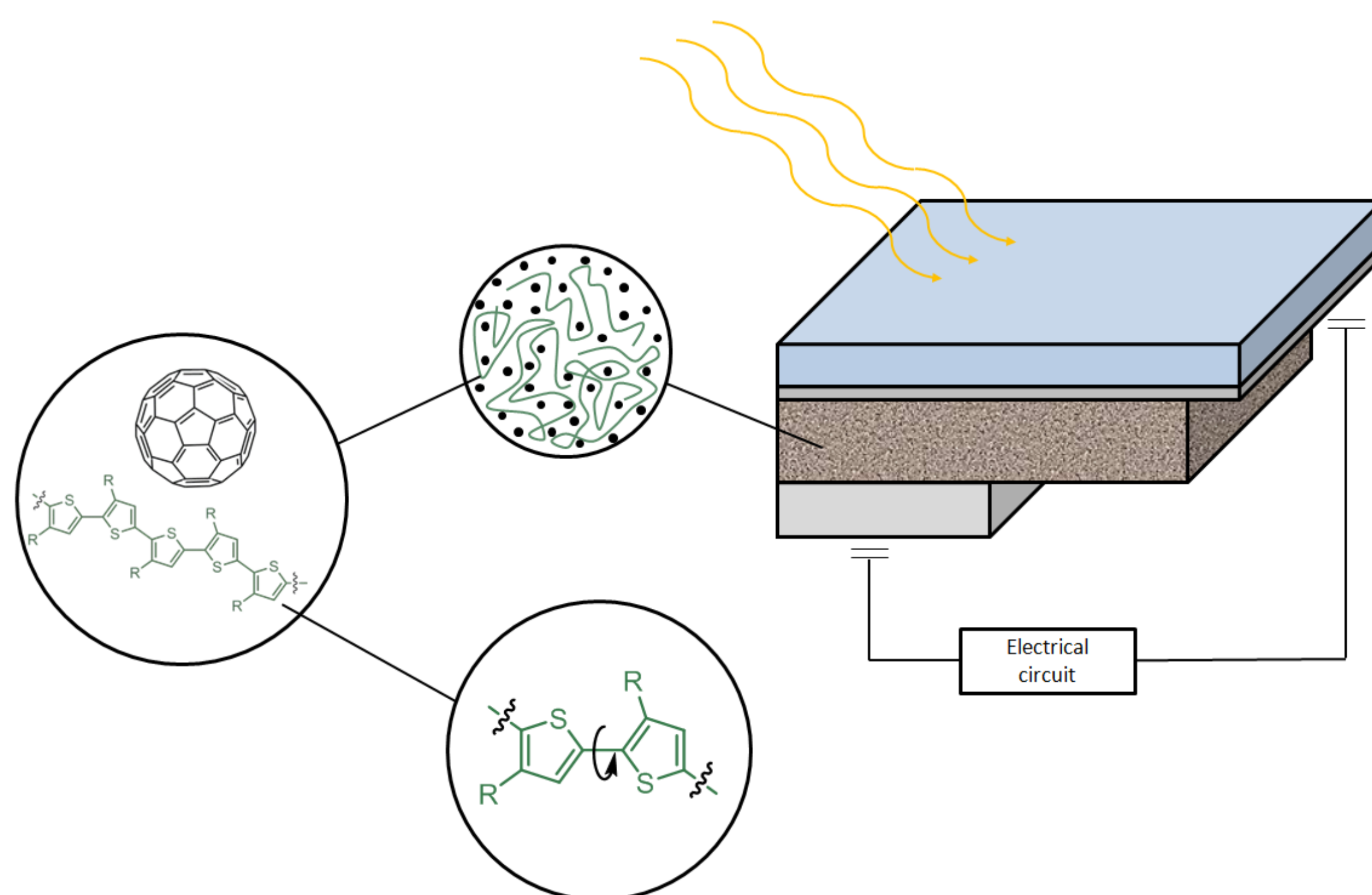
Abstract

The excited state dynamics of polythiophene models were investigated using gas phase Time-resolved Photoelectron Spectroscopy. The results show that the efficient formation of long-lived states is not due to monomer structure. The smallest effective model system was a bithiophene, which showed signs of triplet state formation within femtoseconds. The resulting states were found to live to longer than 400 ps in the gas phase, and shows very different behavior from that in solvent. These results will help unravel which properties of the polythiophenes are intrinsic molecular properties, and which are solvent-molecule interactions.

Introduction

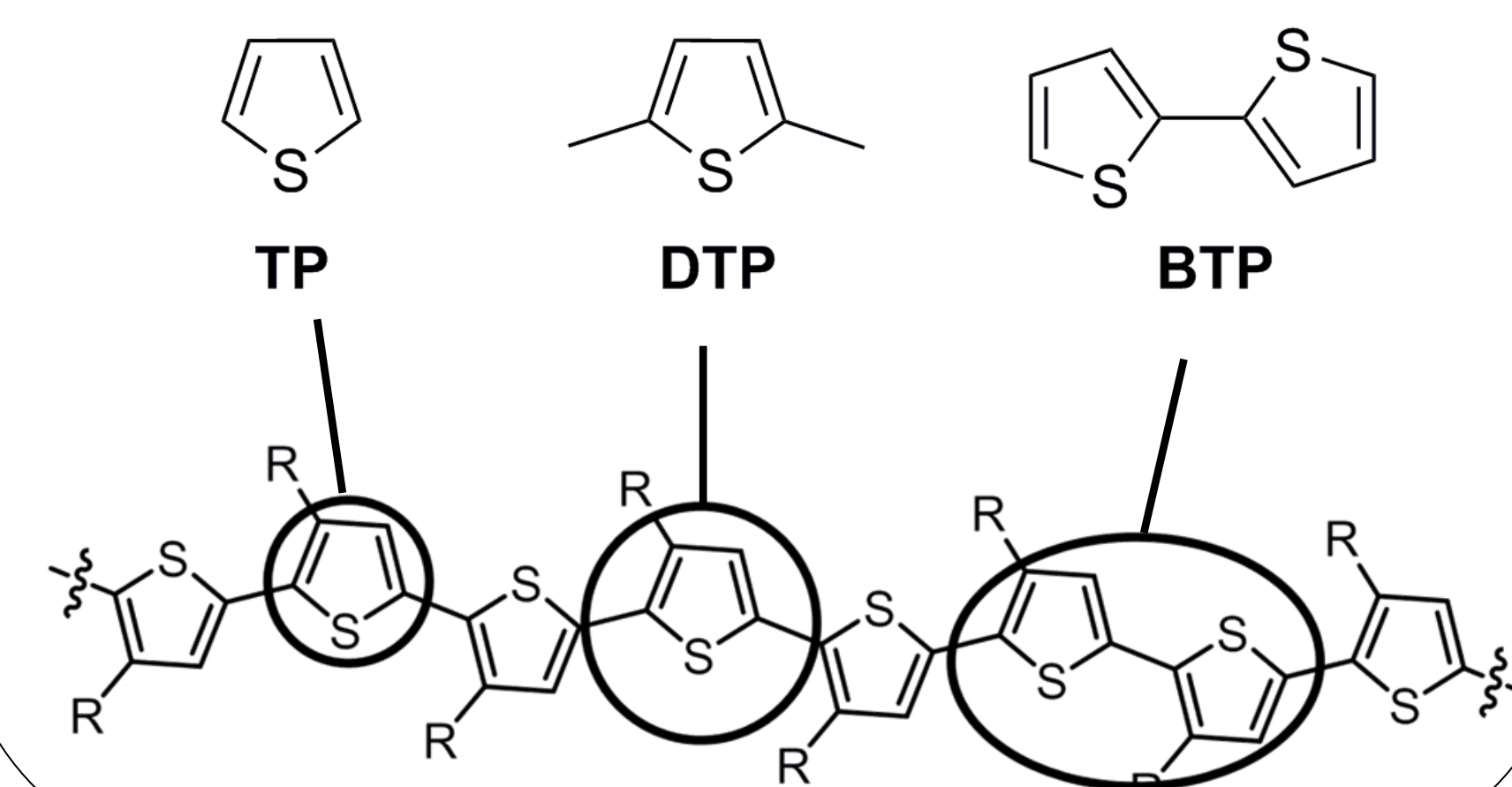
Polythiophenes are ubiquitous in organic photovoltaics (OPVs), playing both the role of chromophore, electron donor and conducting polymer. The ability to generate charge separated states for electrical power depends on the broadness and intensity of electronic transition, and the efficiency with which long-lived states are formed. But does the ability to form long-lived, exploitable states come from the individual monomers or an interplay between several monomers?

For this reason, the structural motif in polythiophenes responsible for generating exploitable, long-lived states is investigated here.

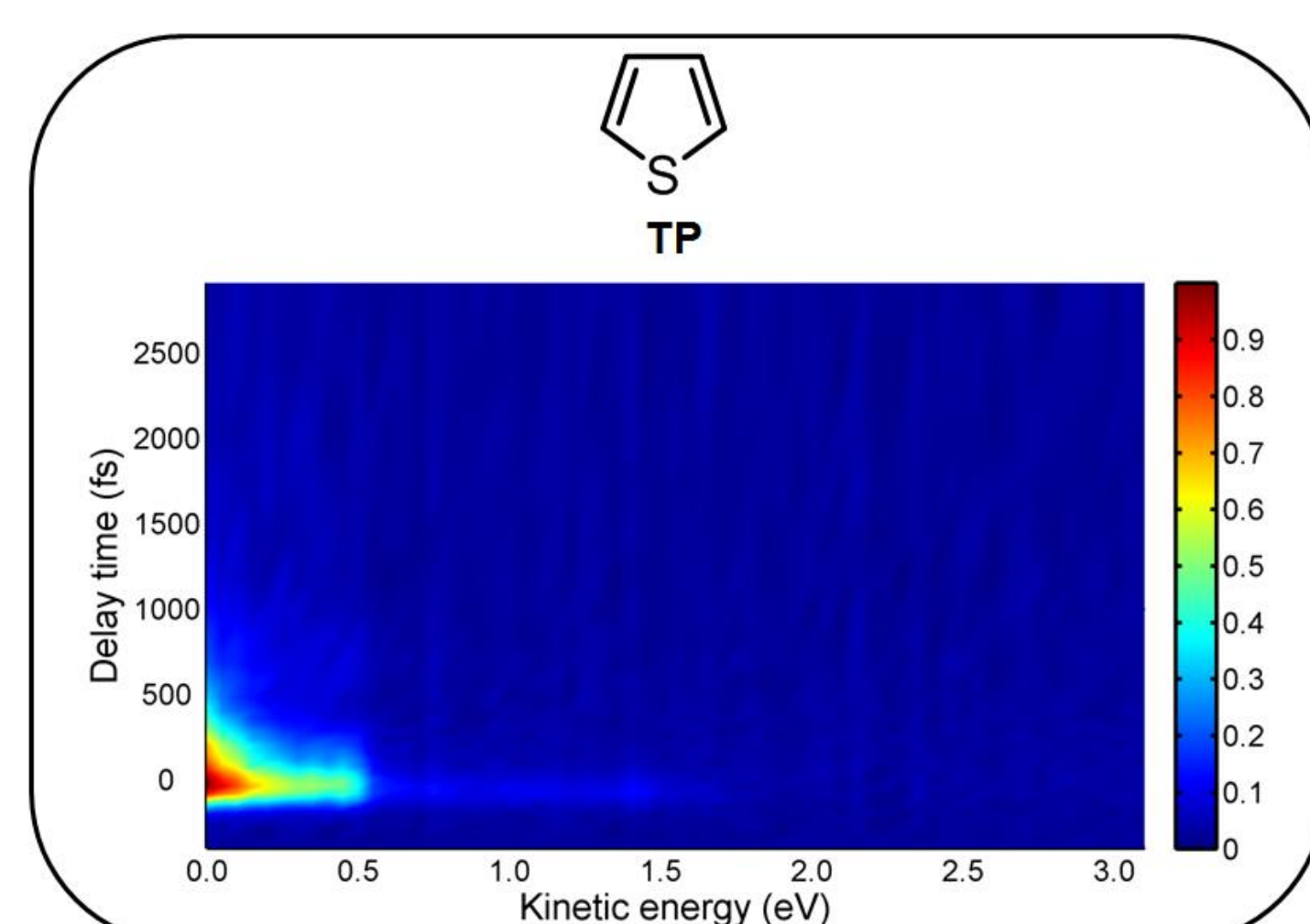


Experimental Setup

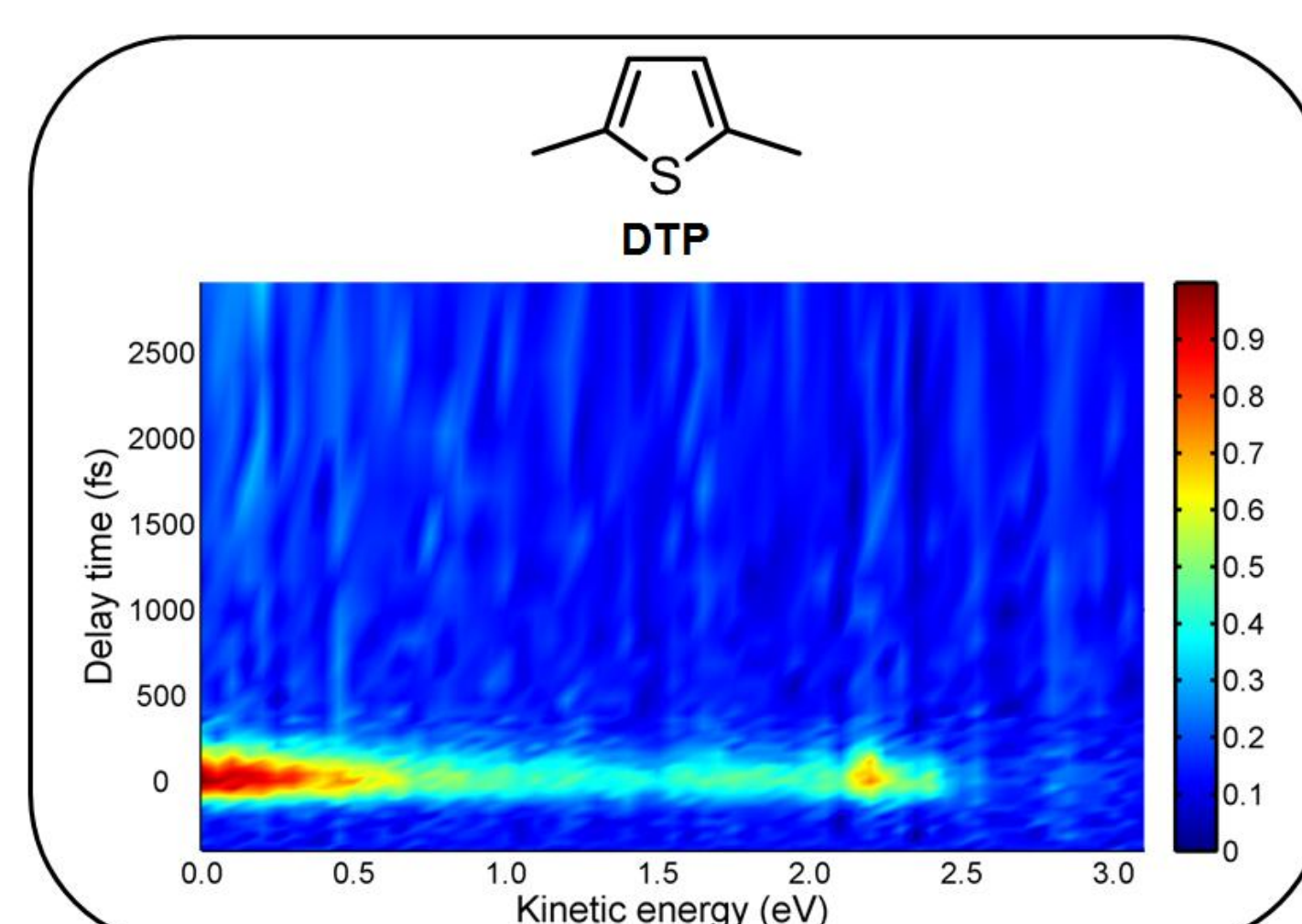
Using Velocity Map Imaging (VMI) we recorded the gas-phase Time-Resolved Photoelectron Spectra (TRPES) of the three compounds thiophene (**TP**), 2,5-dimethylthiophene (**DTP**) and 2,2'-bithiophene (**BTP**), see the main figure. The pump-probe delays were scanned from 0 to 4 ps for **TP** and **DTP** and from 0 to 400 ps for **BTP**. For **TP** and **DTP** a 201 nm pump photon with 280 nm probe photon was used, while for **BTP** a 289 nm probe photon with 400 nm probe through a [1+2']-ionization was used.



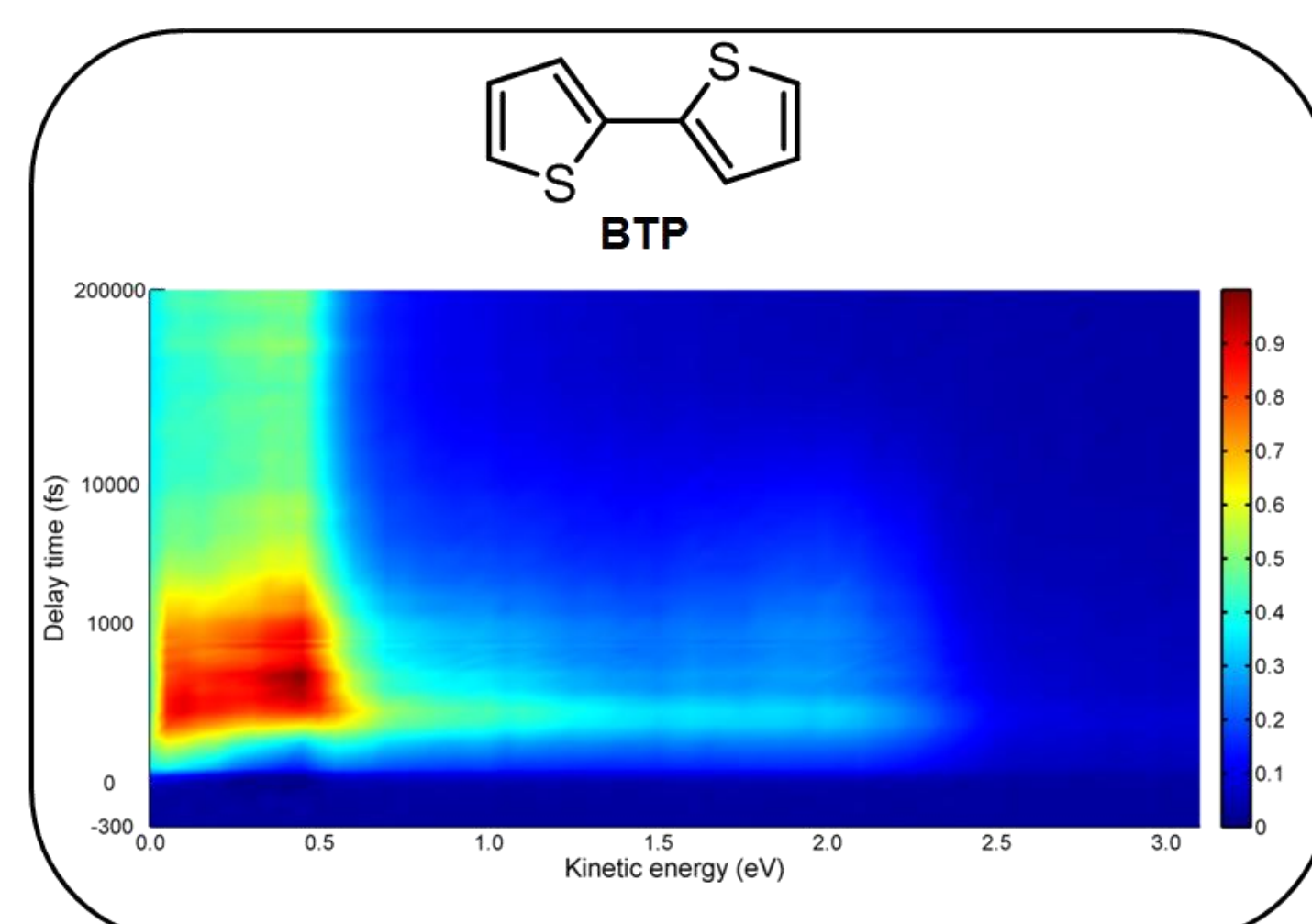
Results



TR-PES: 201 nm pump, 280 nm probe



TR-PES: 201 nm pump, 280 nm probe



TR-PES: 289 nm pump, 400 nm probe

TP and **DTP** does not form any long-lived states (life-times were measured to be 0.3 ps and 0.12 ps respectively, before returning to S_0).

Thus, efficient formation of triplet states does not come from the thiophene monomers alone, or the substitution pattern on the monomers.

BTP showed very efficient formation of triplet states, with the initial triplet states being formed faster than can be resolved with our instruments. The triplets gradually decay into a single state, which was found to live for longer than 400 ps.

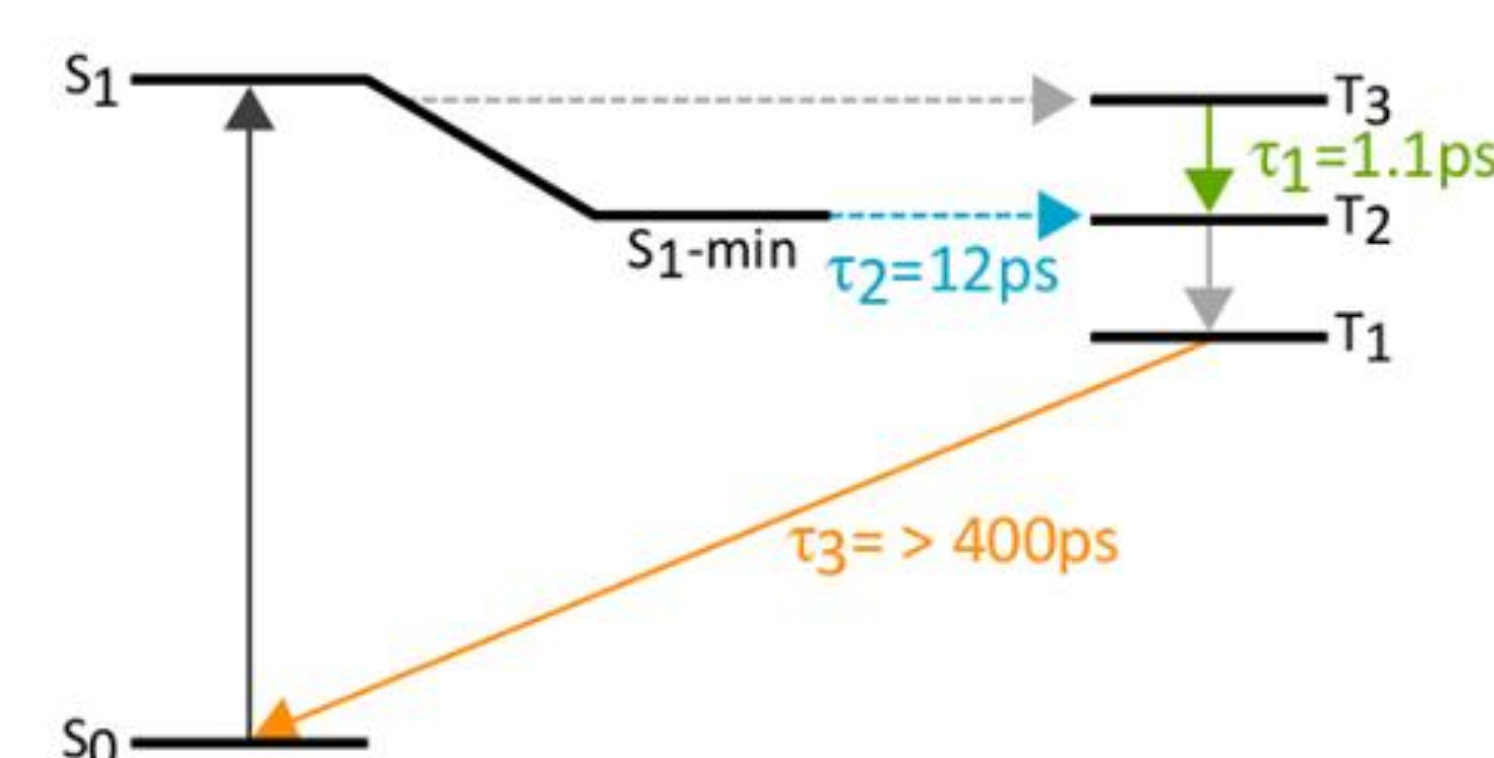
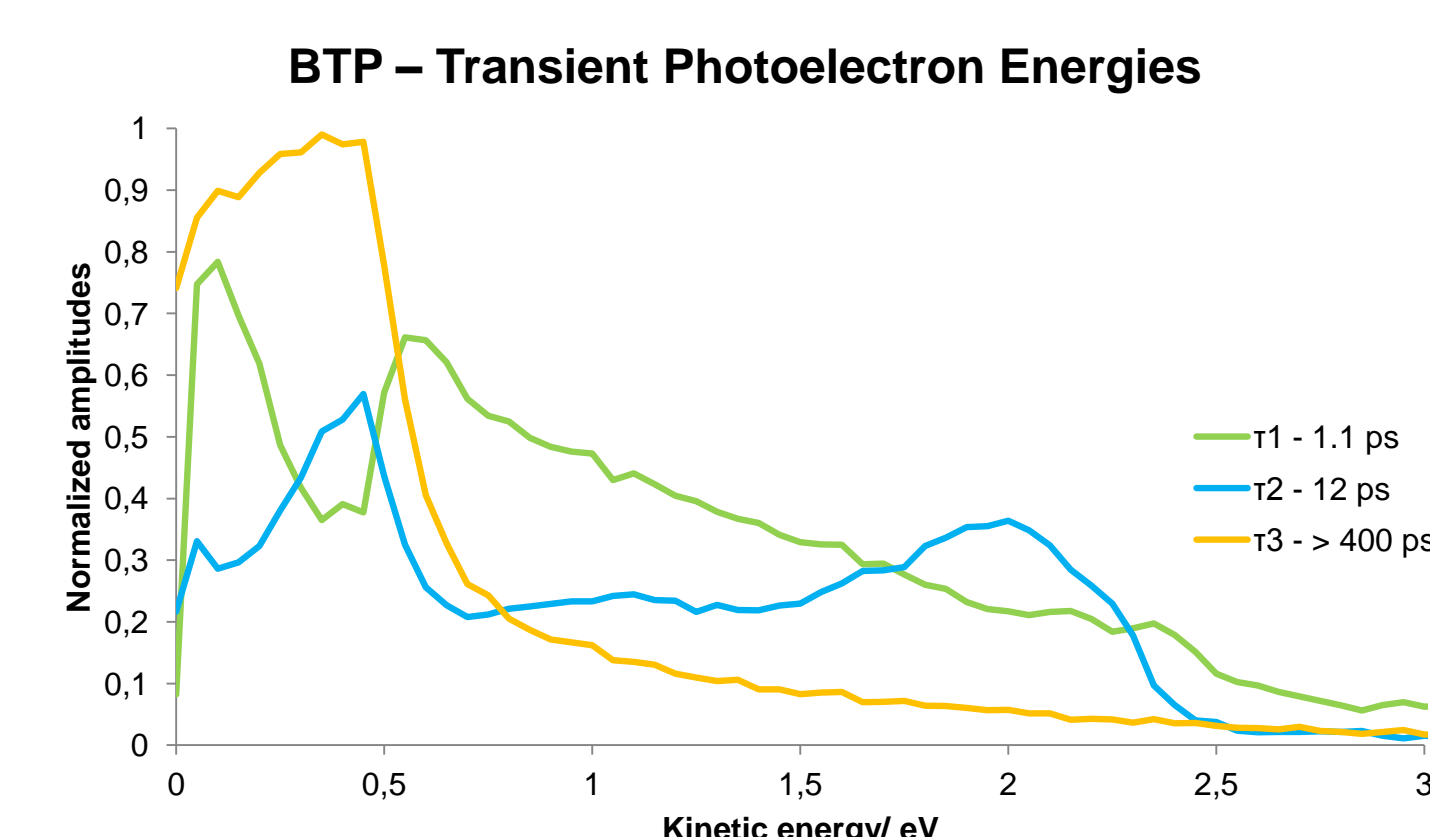
BTP is therefore a good model system for polythiophenes, and shows that the triplet state generation comes from the interplay of two monomers.

Discussion

The very short-lived singlets formed in **TP** and **DTP** are probably due to conical intersections along the C-S bond breaking coordinate. (Weinkauff *et al.*)

In **BTP** the excited molecule is not taken to the C-S bond-breaking region but instead into the ring torsion coordinate, were efficient coupling to the triplet state removes population from the S_1 state (Kölle *et al.*)

The **BTP** TRPES data shows three transients with different decay times. These can be explained by an initial efficient crossing into the triplet states found close to the Franck-Condon region followed by a slower crossing after relaxation, and finally a decay of T_1 , which lives longer than 400 ps.



The formed triplet states live far longer than has been found in solution studies, where the C-S ring opening was found to occur on within tens of picoseconds. The addition of more energy through a 266 nm pump photon instead of 289 nm gave no change in life-time of the triplet state. The decay from T_1 to S_0 must therefore be dependent on solvation to occur efficiently.

Conclusion

The excited state dynamics of polythiophene is derived from neither the monomeric structure nor the substitution pattern, but from the coupling between two or more monomers. This coupling has previously been shown to occur along the ring-torsion coordinate. We hypothesize that once in the triplet state **BTP** is dependent on energy from the environment to reach a conical intersection to revert to the ground state. Further work on this system will include restriction of the ring-torsion coordinate to see whether the efficient crossing is prevented.

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